Fabrication of Ordered Cu₂O Quantum Dot Arrays on SrTiO₃ (100)





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Presentation Outline

Introduction

Why we are interested in $Cu_2O/SrTiO_3$. Why directed self-assembly using FIB.

<u>Experiment</u>

Experiment setup Experiment procedures

Results

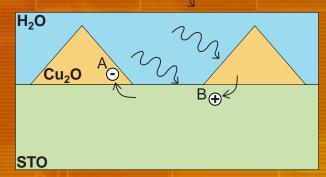
Discussions



Introduction

Why we are interested in Cu₂O/SrTiO₃

- Photocatalytic decomposition of water on Cu₂O interface under visible light irradiation¹.
 - Produce hydrogen for fuel cells
 - High density QD array for maximum device efficiency



A: photo-oxidation (oxygen production)
B: photo-reduction (hydrogen production)

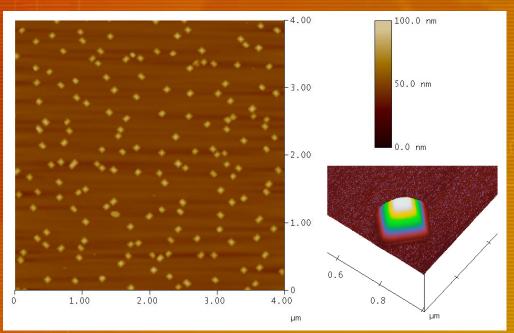
- Quantum dots 0 D, size-dependent optical and electrical properties new applications
 - Cu₂O QDs are expected to be exhibit spatially confined exciton states good candidate to observe Bose-Einstein condensation
 - 1. M. Hara, T. Kondo, M. Komoda, S. Ikeda, K. Shinohara, A. Tanaka, J. N. Kondo, and K. Domen, *Chem. Commun.* 357 (1998).



Introduction

Why we are interested in directed self-assembly of QDs.

- MBE growth of semiconductor QDs for V, III-V, II-VI.
 Oxygen plasma-assisted MBE growth of metal oxide QDs (e.g. Cu₂O/SrTiO₃)
 - Self-assemble on lattice mismatched strain system
 - Quasirandom on planar substrate.

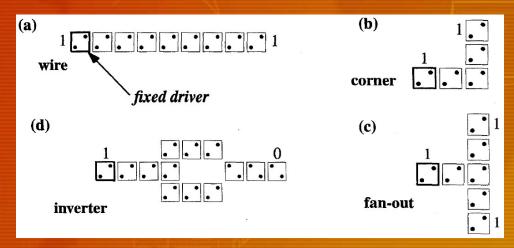




Introduction

Why we are interested in directed self-assembly of QDs.

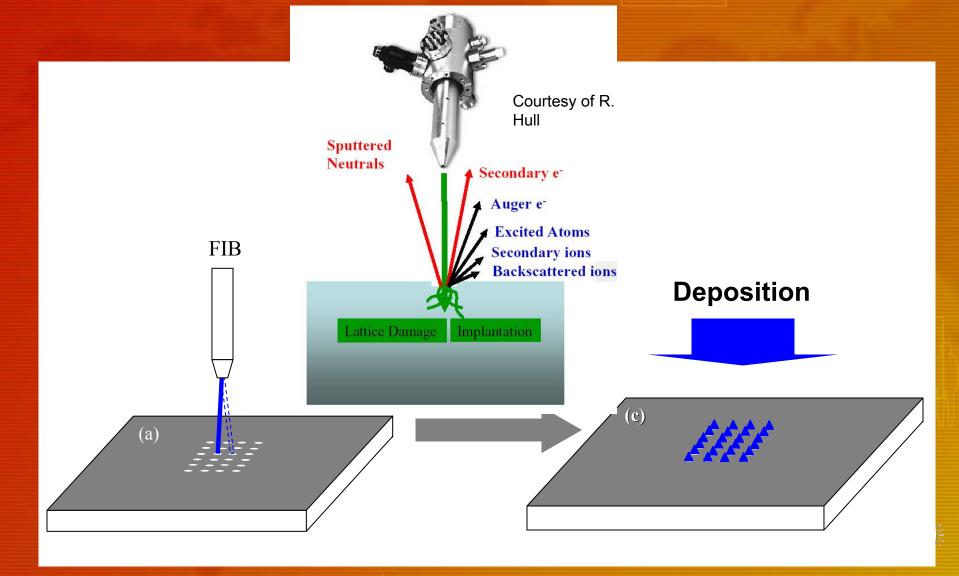
- New nanodevices and new applications
 Size and location control reproducibility
 Ability to join the dots into complex assemblies creates many scientific opportunities.
 - Quantum cellular automata²
 - Quantum dot lasers



2. Porod, W. (1998). Cellular Neural Networks and Their Applications Proceedings, 1998 Fifth IEEE International Workshop, 20.



Experiment expectations



Experiment

SrTiO₃ (001) oxide surface

Surface modification

Technique: FIB Modification

Analysis: AFM

Patterned surface

Substrate cleaning &---annealing

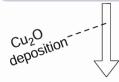
Technique: Surface Preparation

Chemical etching

High temperature annealing

Analysis: AFM

Cleaned surface with FIB patterns



Technique: OPA-MBE QD Synthesis

Analysis: XPS/AES, RHEED

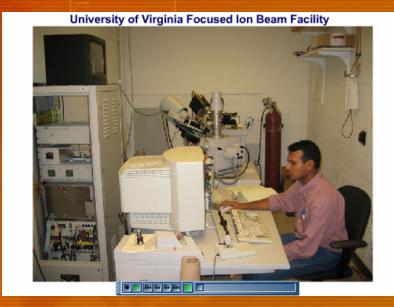
Cu₂O QDs formation on SrTiO₃

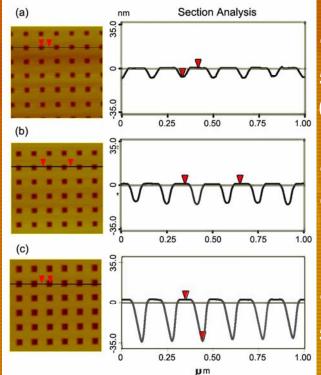


Analysis: HR-XRD, AFM, SEM

First order understanding of how to direct the self-assembly of metal oxide nano-structures

Experiment steps





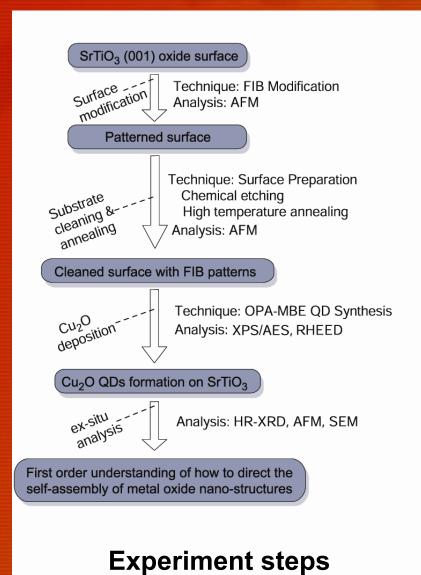
167 nm 5 scans 625x5

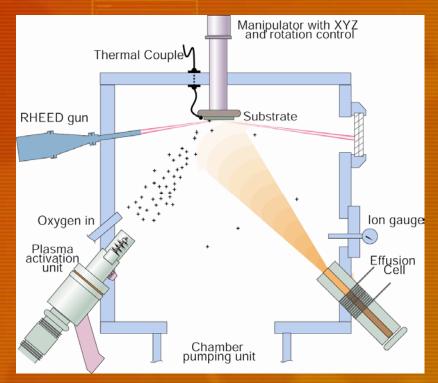
167nm 10,

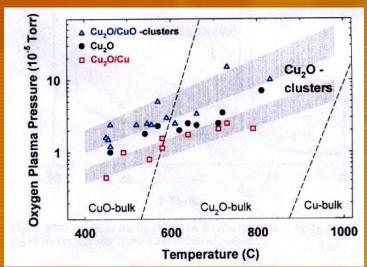
167nm 50



Experiment







As determined by XPS & AES³

3.

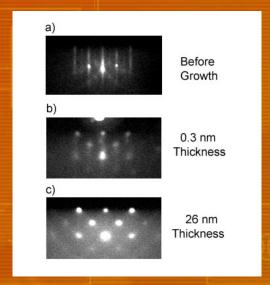
Lyubinetsky, I. et al., (2003). J. Appl. Phys., 94, 7926.

Experiment

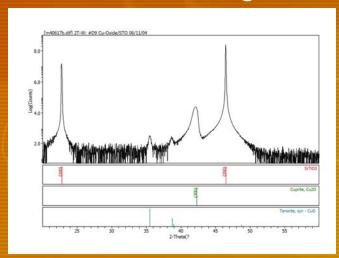
SrTiO₃ (001) oxide surface Surface --Technique: FIB Modification modification Analysis: AFM Patterned surface Technique: Surface Preparation Substrate Chemical etching cleaning & High temperature annealing annealing Analysis: AFM Cleaned surface with FIB patterns Technique: OPA-MBE QD Synthesis CN₂O. deposition Analysis: XPS/AES, RHEED Cu₂O QDs formation on SrTiO₃ ex-situ Analysis: HR-XRD, AFM, SEM analysis

Experiment steps

First order understanding of how to direct the self-assembly of metal oxide nano-structures



V-W growth Without wetting



HRXRD – Epitaxial Cu₂O (100) // SrTiO₃ (100)



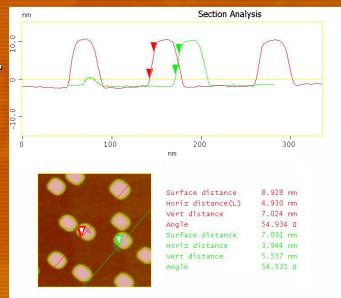
Non-patterned region (Flat SrTiO₃ surface)

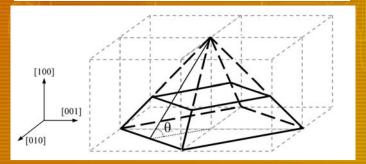
- Shape and size of Cu₂O QDs
 - Weak dependence on thickness init.
 - > Truncated pyramidal crystals
 - {111} side walls with (100) flat tops

Reproducible, stable, epitaxial

- Density of Cu₂O QDs
 - Strong dependence on T
 - Fixed T, close to linear with thickness before coalescence.

To fit the pattern, need to adjust density







Patterned regions: Microscale

- Best result
 - One FIB pit 1-4 nanodot.
 - no islands formed elsewhere

Process conditions:

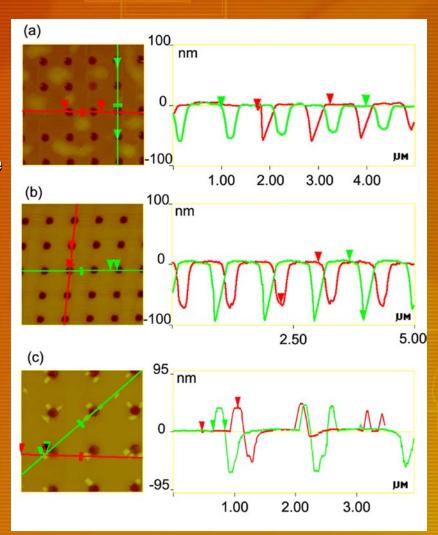
1 um spacing

 $T = 725^{\circ}C$

Thickness: 7 Å

Directions:

- 1. Reproducibility
- 2. Higher integration
- 3. Less surface damage

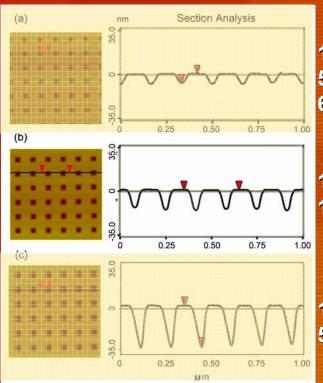


Ga ion density 5.6×10^{18} ions/cm² 4.4×10^{8} Ga ions on each dot



Patterned regions: Nanoscale

- Best result
 - One FIB pit one nanodot.
 - > Few islands formed elsewhere
 - > Larger size, lower height



167 nm 5 scans 625x5

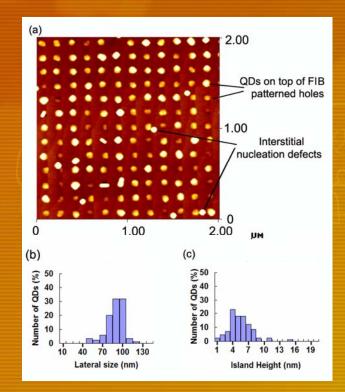
167nm 10,

167nm 50 **Process conditions:**

b) region

T = 700°C

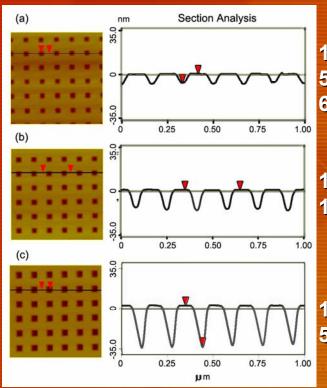
Thickness: 7 Å





Patterned regions

- Comparison results
 - Varying FIB dose
 - Varying spacing



167 nm 5 scans 625x5

167nm 10,

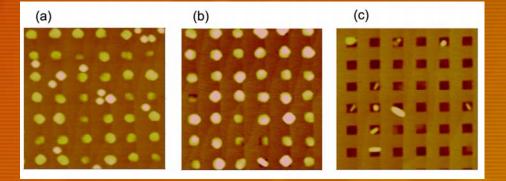
167nm 50

Process conditions:

b) region

T = 700°C

Thickness: 7 Å



- All FIB patterns affected island growth
- Extra islands in (a) while there are still unfilled holes in (c)
 - > volume of pits vs. amount of Cu₂O.



Patterned regions

- Comparison results
 - Varying FIB dose
 - Varying spacing

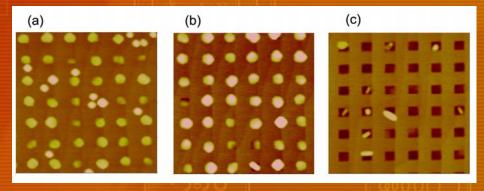
Process conditions:

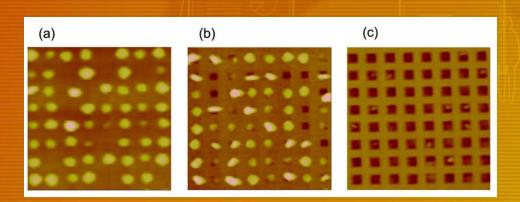
b) region

 $T = 700^{\circ}C$

Thickness: 7 Å

167 nm spacing





130 nm spacing



Patterned regions

- Comparison results
 - Varying FIB dose
 - Varying spacing

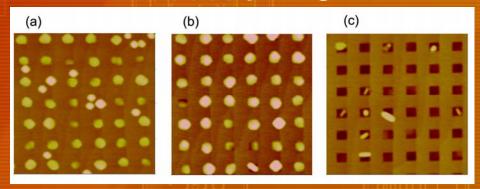
Process conditions:

b) region

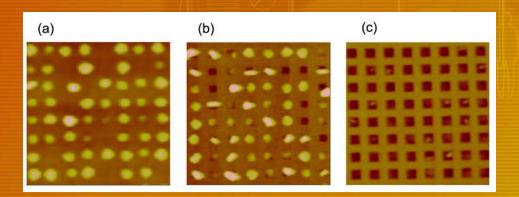
 $T = 700^{\circ}C$

Thickness: 7 Å

167 nm spacing



Extra islands in 167 nm spacing pattern.
Unfilled FIB sites on 130 nm spacing pattern.



130 nm spacing



Patterned regions

- Comparison results
 - Varying FIB dose
 - Varying spacing

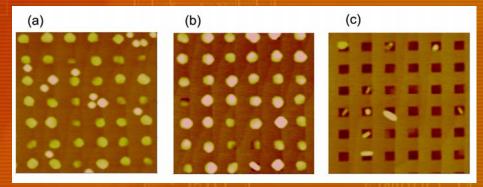
Process conditions:

b) region

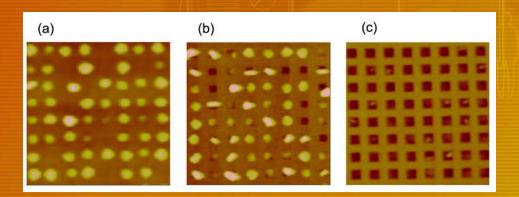
 $T = 700^{\circ}C$

Thickness: 7 Å

167 nm spacing



One to one in 167 nm spacing pattern.
Unfilled FIB sites on 130 nm spacing pattern.



130 nm spacing



Patterned regions

- Comparison results
 - Varying FIB dose
 - Varying spacing
 - Varying thickness
 - Varying temperature More details are discussed in the poster.

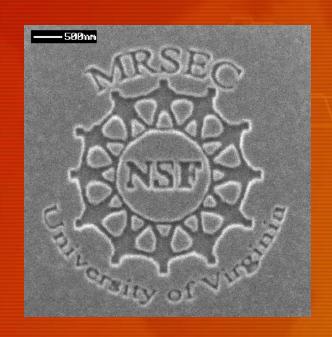


Discussions

- FIB patterning is a successful way to guide the growth of Cu₂O nanodots on SrTiO₃ (100) substrate.
 - Microscale 1:n; Nanoscale 1:1
 - Varying dosage to adjust the pit size
 - Varying thickness to fit different patterns
 - Varying patterns to fit certain density
- Possibility to extend this technique to other material systems
- Detailed growth mechanisms need to be further studied.
 - Ga⁺ effect
 - Topography
 - Local stress/strain
 - Local chemistry



Acknowledgments:



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